Anharmonic rattling vibrations effects in the ESR of Er^{3+} doped SmB_6 Kondo insulator

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(Presented 1 November 2016; received 23 September 2016; accepted 30 October 2016; published online 23 January 2017)

We report X-band Electron Spin Resonance (ESR) experiments on ≈ 0.2% and ≈ 0.7 % Er^{3+} doped SmB_6 at low temperature (4 K - 40 K). The crystal field ground state of Er^{3+} in SmB_6 is a Γ_8 quartet with a nearby Γ_6 excited doublet. The angular dependence of the resonances is not consistent with transitions between pure cubic crystal field states. The data were interpreted in terms of a dynamic Jahn-Teller (JT) effect by a coupling to Γ_3 vibrational modes, which we propose to originate from the rattling of the small Er^{3+} ions in the large SmB_6 cage. Our data show an anisotropic pair of E and E' resonances at $g \approx 4.4$ and two nearly isotropic signals at $g \approx 5.8$, one intense and narrow (A vibrational mode) and the other broad and faint, which we attribute to Er^{3+} ions at lattice sites which are strongly affected by strain, defects and/or extrinsic Al impurities that inhibits the JT effects. Our results are in general consistent with those previously reported by Sturm *et al*. In addition to the angular dependence of the lines, we discuss the intensities, *g*-values and the linewidths of the Er^{3+} transitions as a function of temperature. [http://dx.doi.org/10.1063/1.4974914]

SmB_6 has been predicted[1] to be a strong Topological Kondo Insulator displaying surface dominated conductivity below 4 K.[2,3] SmB_6 is a homogeneously intermediate-valent[4] f-electron Kondo insulator with a small indirect gap of approximately 54 K.[5,6] The origin of this gap is attributed to the coherent hybridization of localized narrow 4f band states with the broad 5d conduction band.[7–10] The topological surface states have been observed in dH-vA quantum oscillations[11] and via ARPES.[12–14] There is also evidence for intrinsic bulk "in-gap" bound states, ascribed to magnetic excitons,[15] from the T-dependence of the optical transmission and reflectivity through films, Raman scattering, inelastic neutron scattering, susceptibility and high field ^{11}B NMR Knight shift and Korringa relaxation measurements.[16,17]

Previous ESR experiments have shown unusual spectra of Er^{3+} in SmB_6 below 4.2 K, i.e., the angular dependence of the resonances was not consistent with pure cubic crystalline field transitions. This result was interpreted in terms of a dynamical Jahn-Teller (JT) effect on the cubic Γ_8 crystal field ground state ascribed to the intermediate valence character of SmB_6.[18,19] In this work we report more detailed X-band ESR experiments on ≈ 0.2 % and ≈ 0.7 % Er^{3+} doped SmB_6 at low-T (4 K - 40 K). We observe an anisotropic pair of resonances at $g \approx 4.4$ and two nearly isotropic signals at $g \approx 5.85$, one intense and narrow and the other broad and faint. We propose, alternatively, that the small Er^{3+} ions experience anharmonic rattling vibrations in the interstitial positions of the large cage rigid lattice host of SmB_6.[20,21] The narrow resonances can be accounted for by the dynamic JT effect due to the coupling of the Γ_3 rattling modes and the Γ_8 crystal field ground state. The broad

line is interpreted as a regular Γ_6 crystal field ground state of Er^{3+} ions located at lattice sites which are strongly affected by strain, defects and/or extrinsic Al impurities that inhibits the JT effects.[22–24] In addition to the angular dependence of the lines, we discuss the intensities, the linewidths and the hyperfine coupling of Er^{3+} as a function of temperature.

$Sm_{1-x}Er_xB_6$ (nominally x_n = 0.01; 0.04) single crystals were prepared by Al-flux technique as described in refs. 23 and 25. The measured crystals were prior treated in a diluted mixture of nitric and hydrochloric acids in ultrasound bath to remove the aluminum flux remaining on the surface of the crystals. The magnetization measurements were performed in a Quantum Design MPMS3 system. The X-band ESR experiments have been carried out in a conventional CW Bruker-ELEXSYS 500 spectrometer using a TM_{110} cavity for the low doped samples and a TE_{102} cavity for higher doped samples. Both cavities have been coupled to an Oxford Instruments helium gas flow temperature controller system.

The magnetic susceptibility of the $Sm_{1-x}Er_xB_6$ (nominal x_n = 0.01) crystal shows a Curie-Weiss behavior at low-T (see Fig. 1). An Er concentration of $x_e \approx 0.002$ was estimated by subtracting the pure SmB_6 contribution and assuming an Er^{3+} oxidation state (inset of Fig. 1). The same procedure used for the x_n = 0.04 sample leads to $x_e \approx 0.007$. The general features of the previous ESR report[18] were reproduced by our experiments, i.e., a strong narrow isotropic resonance at $g \approx 5.85$ ($H_r \approx 1150$ Oe) and two narrow anisotropic resonances around $g \approx 4.4$ ($H_r \approx 1520$ Oe) (Figs. 2a,b). However, our ESR experiment revealed an extra broad and weakly anisotropic resonance superimposed to the previously reported isotropic narrow one at $g \approx 5.8$ ($H_r \approx 1100$ Oe) (Fig. 2b).

The T-dependence of the ESR spectra of Er^{3+} in $Sm_{0.998}Er_{0.002}B_6$ single crystals is shown in Fig. 2c. The lineshape changes dramatically from Lorenztian at 4 K to a metallic Dysonian for $T > 4$ K. This behavior is associated to the appearance of a microwave skin depth effect due to the increasing conductivity of SmB_6 in this temperature range.[6] These results are consistent with the hybridization gap at low-T^2 and the loss of coherence at higher T, when the hybridization gap of SmB_6 starts to close.[8] Therefore, at least below $T \approx 4$ K the Er^{3+} ions are probing the insulating properties of SmB_6.[2]

To investigate the T-dependence of the Er^{3+} ESR spectra and avoid the skin depth effects we have prepared powdered crystals of Er doped SmB_6 ($Sm_{1-x}Er_xB_6$; $x_e \approx 0.002$ and 0.007). Figure 2d shows the T-dependence of the ESR spectra for the $x_e \approx 0.002$ powdered crystals. These spectra present a Lorentzian lineshape in the entire T-range investigated, confirming that the skin depth is larger or at least of the order of the size of the powder grains. In this way the intensity of the signal is not limited by the microwave penetration depth.

The narrow ESR line ($g \approx 5.85$) presents a very well defined hyperfine structure corresponding to the $^{167}Er^{3+}$ (I = 7/2, 23% abundance) isotope (see Fig. 2d). The obtained hyperfine parameter ^{167}A = 74(1) Oe is in good agreement with the value previous reported for Er^{3+} ESR in SmB_6[18] and, within the accuracy of our experiment, it was found to be T-independent.

The T-dependence of the intensity corresponding to the spectra in Fig. 2d, (see Fig. 3a) indicates that the narrow line transition of $g \approx 5.85$ (blue circles) is an excited state at $\approx$ 10 to 15 K above

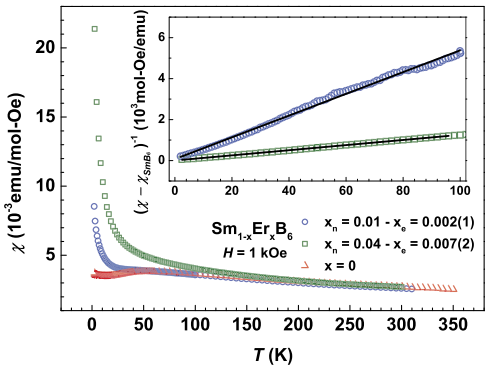

FIG. 1. Thermal dependence of the magnetic susceptibility for Er^{3+} doped and pure SmB_6 single crystals. The inset shows the inverse of the Er^{3+} contribution to the susceptibility and the corresponding linear fit.

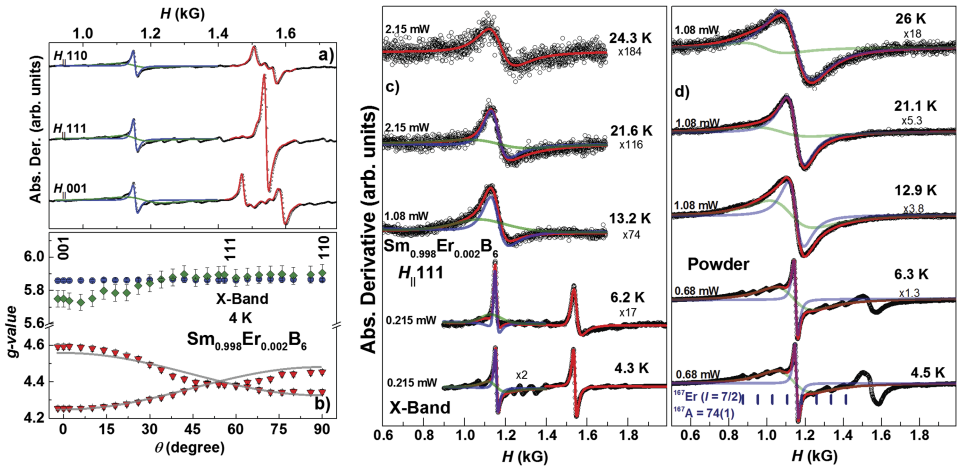

FIG. 2. a) $Sm_{0.998}Er_{0.002}B_6$ single crystal ESR spectra as function of the orientation of the applied magnetic field at 4 K. b) g-value angular dependence in the [110] plane at 4 K. The color of the lines in a) indicates the correspondence between the lines and their associated g-values in b). The solid gray lines in b) are the fit described in the text. Thermal dependence of ESR spectra of $Sm_{0.998}Er_{0.002}B_6$ c) H||[111] single crystal and d) powdered sample. The microwave power and the scaling factor are indicated in each spectrum. The solid lines in the panels c) and d) are the fits of the three distinct resonance lines. The series of short vertical blue lines under the 4.5K spectrum in d) indicates the transitions associated to the hyperfine splitting of the ^{167}Er (I = 7/2, 23% abundance) isotope.

the ground state. Similar results were obtained for the powdered crystals of $x_e \approx 0.007$ (see Fig. 3b). The T-dependence of the intensity corresponding to the broad line, superposed to the narrow one at $g \approx 5.8$, presents a Curie-like behavior down to our lowest temperature of 4 K (see Figs. 3a,b). Similar Curie-like T-dependence of the intensity was found for the anisotropic resonance with $g \approx 4.4$ (see Figs. 3a,b). Therefore, the broad resonance at $g \approx 5.8$ and the narrow pair of lines at $g \approx 4.4$ correspond to ground states.

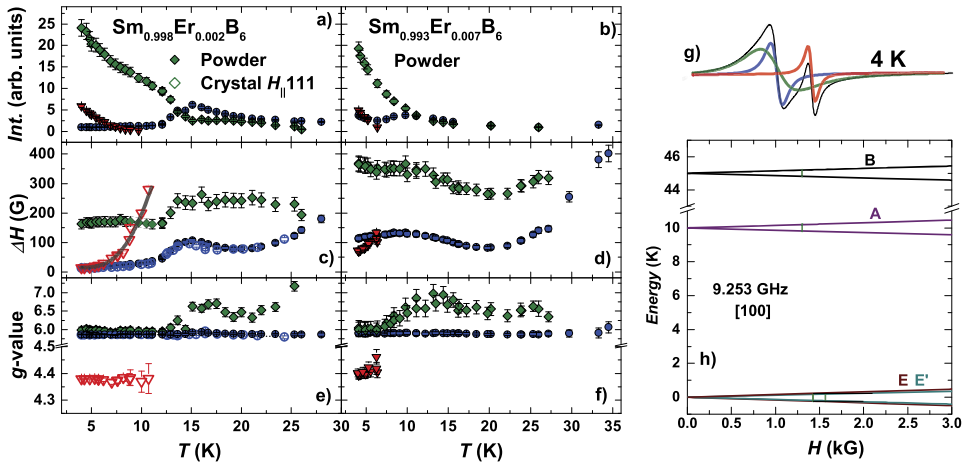

FIG. 3. T-dependence of the a), b) intensity, c), d) linewidth, and e), f) g-value associated with the ESR spectra of $Sm_{0.998}Er_{0.002}B_6$ and $Sm_{0.993}Er_{0.007}B_6$, respectively. The filled and open symbols correspond to powdered and H||[111] single crystal ESR spectra, respectively. In g) a 4 K ESR spectrum is shown for the powdered $Sm_{0.993}Er_{0.007}B_6$ sample; the color of the fittings indicates the correspondence between the lines and their symbols. The solid line in c) is the linewidth fit assuming a Korringa and an activation energy relaxation mechanisms: $\Delta H = \Delta H_0 + bT + A\exp(-\Delta/T)$, where ΔH_0 is the residual linewidth, b is the Korringa ratio, A is a constant and Δ is an activation energy. h) E, E', A and B vibronic doublets as a function of a magnetic field along the [100] direction. The excitation energies of the A and B levels are assumed 10 K and 45 K, respectively. The vertical green lines represent the transitions for a typical X-band frequency.

The narrow resonances in the $Sm_{0.998}Er_{0.002}B_6$ sample present an exponential-like thermal broadening of the linewidth indicating relaxation via thermally populated excited states (see Fig. 3c). A similar but not so clear broadening was observed for the $Sm_{0.993}Er_{0.007}B_6$ samples due to the much broader residual linewidths (see Figs. 3c,d). However, an anomalous "bump-like" broadening of the linewidth is observed around 15 K on both, narrow and broad, $g \approx 5.8$ resonances. Within the accuracy of our experiments the measured g-values were T-independent (see Figs. 3e,f).

We suggest that the dynamic JT effect (weak JT-coupling), in terms of the tunneling model,[18,19,26,27] is perfectly applicable to the anharmonic Er^{3+} rattling vibrations model and capable of explaining the splitting of the anisotropic narrow resonances at $g \approx 4.4$. The T-dependence of the intensity for these resonances indicates that they belong to a ground state (see Figs. 3a,b). However, the peculiar anisotropy observed for these resonances indicates that they are not transitions within a regular Γ_8 crystal field ground state as may suggest the Lea-Leask-Wolf diagram for $J = 15/2$, $W < 0$ and $x \approx 0.8$.[28] Therefore, we propose that the $g \approx 4.4$ transitions belong to a new doubly degenerate (E,E') 'vibronic' JT ground state and the ESR spectra of Er^{3+} in SmB_6 have to be analyzed following Ham.[26] Figure 3g shows the E, E', A and B vibronic states originated from the coupling of the crystal field quadruplet to the vibrational rattling modes, $\Gamma_8 \otimes \Gamma_3$, as a function of the applied magnetic field. The angular dependence of the narrow $g \approx 4.4$ pair of resonances can be fitted by the expected E, E' g-value angular dependence (Eq. 34 of Ref. 26, see Fig. 2b).

Within this scenario, the observed T-dependence of the intensity for the isotropic narrow (17 G) resonance observed at $g \approx 5.85$ indicates that it would correspond to the first excited 'vibronic' (A) JT Kramers doublet at ≈ 10 K above the ground states (see Fig. 3g). Moreover, the thermal broadening of the linewidth for the $g \approx 4.4$ resonances and the narrow one at $g \approx 5.85$ indicates relaxation via excited states for $T > 4$ K (see Fig. 3c). The broadening of the $g \approx 4.4$ line was fitted by a combination of Korringa (linear in T) and an exponentially activated mechanisms (see Fig. 3c). A negligible Korringa parameter, $b = 0.1(2)$ G/K, $A = 1.6(6)\ 10^4$ G and an activation energy of $\Delta = 45(3)$ K were obtained from the fit. It is possible that the excited vibronic state B could be the main relaxation channel for the E and E' doublet. This relaxation process may be mediated by phonons (Orbach mechanism[29]) or conduction electrons (Hirst mechanism[30]). Since both relaxation mechanisms lead to an exponential-like dependence of the linewidth, it is not possible to distinguish whether phonon or conduction electrons mediate the relaxation process. It is worth mentioning that intermediate-valence relaxation mechanism[31] could also give a similar thermal dependence of the linewidth. The Er^{3+} impurities and other possible Sm vacancies in our samples are expected to create an impurity band inside the gap of SmB_6.[24,32] The "bump-like" broadening of the linewidth observed around 15 K in both, narrow and broad, $g \approx 5.8$ resonances could be attributed to the population of the impurity band as the temperature increases leading to an exponential contribution to the relaxation at higher-T. Nevertheless, we can not rule out that a magnetic coupling between the Er^{3+} and the Kondo Sm^{3+} ions can give a non-trivial temperature dependent contribution to the relaxation process.

In summary, our ESR experiment of Er^{3+} in SmB_6 confirms the Sturm *et al.*[18] results on the splitting and anisotropy of the resonances observed at $g \approx 4.4$ which are associated to the split-off 'vibronic' (E,E') JT Kramers ground state doublet. The narrow isotropic resonance at $g \approx 5.85$ is attributed to the split-off 'vibronic' (A) JT Kramers excited doublet at ≈ 10 K above the ground state. We propose that the origin of the E, E', A and B ground and excited 'vibronic' states is the rattling of the relatively small Er^{3+} ions in the large SmB_6 cage. The resonance of the B state, around 45 K above the ground state, was not observed in our experiment. In addition, we have observed a broad and weakly anisotropic resonance at $g \approx 5.8$ regular Γ_6 crystal field ground state which we attribute to unaffected JT Er^{3+} ions due to the presence of strains, defects, vacancies and/or extrinsic Al impurities that inhibits the JT effects.[22–24] Note that the Γ_6-doublet does not couple to Γ_3 vibrational modes. Note that the residual linewidth for the $x \approx 0.007$ sample is much broader than that for the sample of $x \approx 0.002$ sample (see Figs. 3c,d). It is worth mentioning that Dy^{3+} and Nd^{3+} doped SmB_6 crystals were also investigated in this work but they did not present significant ESR signal.

This work was supported by the auspices of FAPESP (Grant Nos. 2011/01564-0, 2012/04870-7, 2012/05903-6, 2011/19924-2, 2013/17427-7), CNPq, FINEP and CAPES (Brazil). ZF is supported by the US NSF (Grant No. DMR-0801253) and PS by the US DOE (Grant No. DE-FG02-98ER45707).

Work at Los Alamos National Laboratory (LANL) was performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering. PFSR acknowledges a Director's Postdoctoral Fellowship through the LANL LDRD program.

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